Response to Anonymous Referee #1 comments

The authors present an analysis of submicron aerosol composition, CCN activity, and light scattering measurements made in the Eastern Mediterranean in 2012. They use the available data and modeling techniques to infer aerosol liquid water content and aerosol pH for the submicron aerosol fraction. Given the limitations of the dataset, specifically the absence of gas-phase NH3 data for most of the measurement period, the analysis is consistent with the state of the art. Daily PM10 filter composition analysis was also performed and this information was used to calculate LWC and pH for PM10. I believe this manuscript is publishable in ACP after the following points are addressed directly in the revised manuscript.

Response: *We thank the anonymous referee for the thoughtful review. Most of the issues raised were also concerns of the anonymous referee #3 therefore we have further elaborated on these points in the revised manuscript.*

1) More discussion of the error introduced to the pH estimate by the absence of NH3 (g) data is required. I will note that the "spot check" comparing the ISORROPIA predicted NH3 (g) and the available measurements of NH3 (g) mentioned at the end of section 2 is reassuring, but this discussion should be expanded and more technical information provided for the reader.

Response: *.To address the issue that is also raised by anonymous referee #3 (see also extensive reply to reviewer #3 general comments) a sensitivity study was performed and the more important findings will be clearly stated in the revised version of the manuscript. By adding different amounts of gas-phase ammonia to the initial results and computing ammonia's impact on predicted pH, we show that adding an amount of 5* $\mu g\ m^{-3}$ *of gas-phase ammonia that is an extreme upper limit for ammonia concentrations in the studied region, pH values differ by a maximum of 1 unit (1.4 vs 2.4). Based on climatology data from the area (3-year study of Kouvarakis et al. 2001) gas phase ammonia ranges from 0.02 to 1* $\mu g\ m^{-3}$ *with a mean and median value of 0.32 and 0.28* $\mu g\ m^{-3}$*, respectively, which is even lower than the lowest added amount in the sensitivity study. Therefore the fact of neglecting the gas phase in the calculations has a difference of around 0.5 units in the pH (from 1.38 to 1.85 median values).*

This comment has been addressed in Section 2.4, pages 24-25, lines 901-930 of the current file.

2) More information needs to be provided regarding the LWC and pH analysis for PM10, including a frank assessment of the error bars on the pH and LWC calculations for PM10. I did not see any of this mentioned in section 2, and PM10 is mentioned only briefly at the beginning of section 3.4. The difference in available data and the level of analysis performed on the PM10 vs. PM1 needs to be discussed, especially since these datasets are discussed in conjunction in the later sections of the paper, and given the emphasis in the paper on bioavailability of mineral dust nutrients.

Response: *We agree that the* PM_{10} *results are subject to more uncertainty, as the inorganic semi-volatiles are not in equilibrium. With this said though, the liquid water does equilibrate rapidly and the ionic species therein – hence the calculations provided can be used as an indication of the coarse mode acidity with respect to the fine mode. This will be clearly stated in the revised version of the manuscript. Added information in the methodology section will include the differences in available data for the* PM_1 *and* PM_{10} *fractions.*

This comment has been addressed in Section 3.4, page 30, lines 1062-1069 of the current file.

TABLE 1 -

The error bars on pH values listed here seem to be misleadingly small if the analysis itself introduces at least unit error to the pH estimates for submicron aerosol. How were they calculated for PM1 and PM10?

Response: *We understand that the standard deviations (SD) of the pH estimates appear small and seem not to reflect the error introduced by the absence of gas phase ammonia data. Nevertheless, the variance of the values is expected to be different than the method bias. A clarification will be added in the text that apart from the standard deviation there is also the additional bias that is not expressed in the SD. Furthermore, the source/region data correspond to 7 or 9 days of selected data, representative of these sources/regions. As Finokalia* PM_1 *aerosol contains a considerable amount of sulfates that does not vary significantly with day for the whole time period studied (June-November 2012), this is expected to limit the variance of the estimates. From long-term measurements of the aerosol -composition at the site, the relative contribution of the main* PM_1 *constituents, including ammonium, is quite consistent over the years (e.g., Mihalopoulos et al., 1997; Kouvarakis et al., 2001; Sciare et al., 2003; Koulouri et al., 2008, Bougiatioti et al., 2009; 2011; 2013). A fluctuation of 10-20% in sulfate and/or ammonium concentrations is not expected to be reflected in a pH change, given the logarithmic scale of the property. On the other hand,* PM_{10} *pH estimates express the bulk acidity that covers a wider range.*

FIGURES -

The time series presented in Figures 1 and 2 are not easily legible in the current format, these figures should be redesigned in order to have more meaning for the reader.

Response: *Both figures are now converted to a stacked format on the same scale and are easier for the reader to follow.*

Figures 1 and 2 are now presented for the same time period, using a stacked format.

Response to Anonymous Referee #3 comments

This manuscript reports an analysis of the liquid water content (LWC) and acidity of submicron aerosol sampled in the eastern Mediterranean region during late summer and autumn 2012. Results are interpreted in the context of source region and associated implications for nutrient availability and primary productivity in the eastern Mediterranean region. The topic is relevant for publication in ACP, the investigation utilized state-of-the-science instruments and thermodynamic-model calculations, and results are interesting. Unfortunately, as summarized below, the manuscript suffers from several important shortcomings.

***Response:** We thank the reviewer for the well-articulated and thoughtful arguments that helped improving the presentation of our results, in particular the associated uncertainties and the manuscript as a whole. We have revised our manuscript in view of the reviewer's concerns and have shown that the pH estimates are reliable and with a constrained level of uncertainty and bias. We have further elaborated on these points in the revision for clarity. Below is a point-by-point response (in italics) to the comments raised by the reviewer.*

During most sampling periods, the authors did not generate the gas-phase data required to reliably estimate aerosol-solution pH using the ISORROPIA-II thermodynamic model run in the "forward" mode.

***Response:** Having the gas and aerosol phase measurements indeed provide the least uncertain pH estimates (Hennigan et al., 2015). However, using only aerosol-phase concentration in a forward partitioning calculation can still yield useful pH calculations (e.g., Guo et al., 2015). We evaluate whether this is the case in our data with two approaches: (i) when gas and aerosol data are available, we first test the ability of ISORROPIA-II to reproduce the observed partitioning of inorganic semi-volatiles; the same data are then used to quantify the shift in pH when gas-phase concentrations are omitted from the calculations. (ii) when gas-phase data are not available, thermodynamic calculations are carried out with the observed aerosol composition data in combination with climatological values of gas-phase species (NH_3 and others). The shift in aerosol pH between zero and high concentrations of gas-phase volatiles is then quantified as the upper limit in bias. Both methods are used in this study.*

In addition, as described in more detail below, the authors' estimate of 1 pH unit as a reasonable upper limit for the associated bias is unconvincing.

The method (i) described above was used to estimate the bias in the original submission. We have also used method (ii) to calculate another estimate in the bias and we find that the pH bias does not exceed one unit. Thus, based on these two approaches we can state that 1 pH unit is actually a generous estimate of the bias. The actual upper limit is almost certainly greater than 1 pH unit and, based on results from other coastal locations [e.g., Smith et al., 2007, JGR], the magnitude of bias would be expected to vary significantly as a function of air mass history and time of day. Consequently, it is impossible to differentiate variability in pH associated with the magnitude of bias versus variability driven by environmental factors. Because the calculated pHs for most periods are not representative of those for ambient aerosol and the associated uncertainties are largely unconstrained, these calculated values cannot be reliably interpreted and should not be reported.

***Response:** We agree with the reviewer that the bias is not constant and that all coastal sites do not behave similarly. Our analysis of Finokalia data focuses primarily on the fine (PM1) fraction and shows that the thermodynamic model reproduces the ammonia partitioning when available, and that derived pH values are well within other pH studies for the fine fraction, including Keene et al. (2004). Finokalia PM1 aerosol contains a considerable amount of sulfates, that does not vary considerably with day for the whole time period considered in this study (June-November 2012; see figure below, also provided in the supplementary material). From long-term measurements of the aerosol -composition at the site, the relative contribution* *of the main PM_1 constituents, including ammonium, is quite consistent over the years (e.g., Mihalopoulos et al., 1997; Kouvarakis et al., 2001; Sciare et al., 2003; Koulouri et al., 2008, Bougiatioti et al., 2009; 2011; 2013). A fluctuation of 10-20% in sulfate and/or ammonium concentrations is not expected to be reflected in a pH change, given the logarithmic scale of the property. Given the above, the low concentration of other non-volatile ions (such as Na, K, etc.), and that we are far away from local sources that induce external mixing, the submicron aerosol at Finokalia is internally mixed, highly acidic, and varies slowly with time and hence in equilibrium with the gas phase. Similar conclusion that particles were internally mixed and liquid, has been reached by Hildebrandt (ACP, 2010) based on one month intensive observations with AMS at Finokalia in May 2008. Our findings also imply that the ammonia measurements available for the short period are representative of the whole studied period – as the NH_4^+ record does not indicate considerable fluctuations. Therefore, it is expected that ISORROPIA II is able to capture fine pH in our study, with a constrained level of uncertainty when not using gas-phase NH_3, that is estimated to be less than 1 unit of pH.*

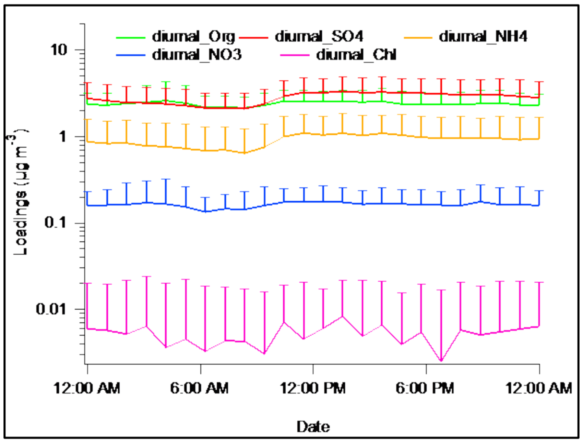

Figure S4: Mean diurnal variability of the main non-refractory aerosol constituents over the studied measurement period (Aug-Nov 2012).

All the above comments, regarding the uncertainties in pH calculations are addressed in detail in Section 2.4 of the revised manuscript, pages 24-25, lines 901-930 of the current file.

Some of the measurement techniques and associated approaches for interpreting results are not described in the methods section and virtually no information on data quality (detection limits, precision, absolute accuracy) is reported. All methods should be described and information on corresponding data quality should be added.

***Response**: We thank the reviewer for pointing out this omission. Short descriptions about the wet annular denuder (WAD) for the gas phase measurements and the ion chromatography analysis are added in the instrumentation section. In addition, information on detection limits and precision for the various techniques applied here, is added in the revised text.*

The methodology section now features the measurement techniques and approaches that were not described, Section 2.2 page 21 and lines 792-795 of the current file.

The analysis is based primarily on the bulk, ionic composition of particles less than 1μm diameter. However, as noted by the authors, mineral aerosol mass and associated liquid water is typically dominated by supermicron diameter size fractions [also see Arimoto et al., 1997, JGR; E. Reid et al., 2003, JGR]. For particles less than 1 μm diameter, dust concentrations decrease with decreasing size [e.g., Reid et al., 2003] whereas aerosol solution acidity typically increases with decreasing size [e.g., Keene et al., 2004]. Consequently, acidities based on the bulk composition of submicron aerosol may not be directly relevant to the acidities for the upper end of the submicron size distribution in which most of the submicron dust resides. In addition, the acidities of submicron aerosol size fractions are typically much greater than those of the super micron size fractions with which most of the mineral aerosol mass is associated. It is evident that, even if the pH estimates were reliable, they would not be directly relevant to pH-dependent processes including nutrient availability involving most of the mineral aerosol, which is a major focus of the analysis.

Response*: We agree with the reviewer that there is a strong link between aerosol pH and aerosol size distribution due to the chemical composition changes with changes in the aerosol size. However, by definition atmospheric aerosol science needs to consider population characteristics and thus is grouping atmospheric aerosols in size bins or in modes. Higher size resolution considered is leading to higher accuracy in the pH calculations. A comment in this respect has been added in the manuscript. We actually show that the acidity of the PM10 fraction is quite different from the acidity of the PM1. It will be also emphasized in the manuscript that* PM_{10} *pHs are qualitative, owing to the external mixing of the aerosol. Using the same acidity for PM1 and PM10 aerosols is wrong and would clearly lead to large biases in predicted nutrient solubility. However, it is not obvious that the nutrient flux from the fine mode is negligible either; the flux is certainly smaller than in the coarse mode – but it can transport much farther away from source regions before deposition, and be considerably more acidified (hence bioavailable). In reality the relative contributions of fine and coarse mode aerosol to the nutrient fluxes are best assessed by comprehensive atmospheric models that consider all the relevant processes from emission to deposition. These points are now better emphasized in the revised manuscript.*

Finally, the pH of PM10 aerosol sampled in bulk is not conservative. Sampling chemically distinct size fractions of PM10 in bulk typically drives significant artifact phase changes of compounds with pH dependent solubilities because the pH of the bulk mixture is different than that of the size fractions with which these compounds partition preferentially in ambient air. Consequently, aspects of the manuscript involving interpretation of acidity based on PM10 composition are inherently problematic.

Response*: The composition of particles less than 1 μm diameter are not subject to filter artifacts as it is provided by the ACSM, for the non-refractory submicron aerosol.* PM_1 *calculations are all based on ACSM measurements and respective* PM_1 *ionic concentrations for cations such as* Na^+*,* Ca^{2+}*,* Mg^{2+}*, corresponding to the fine fraction which is in equilibrium. Therefore, the corresponding submicron acidity is quantitative and succeeds in reproducing the partitioning of ammonia in the gas phase. We completely agree with the reviewer that, on the other hand, the* PM_{10} *results are less quantitative than the* PM_1 *results as obviously particles are not in equilibrium. We can still say however that the coarse mode pH is higher compared to the fine mode pH, especially during periods with a high sea-salt and dust influence. We will make it clear and emphasize it in the revised version of the manuscript.*

The comments above, regarding the pH calculations of the PM_{10} fraction are addressed in Section 3.4, page 30 and lines 1062-1069 of the current file.

Specific Comments

Abstract, line 1. It is unclear what is meant by “drives the aerosol phase.” Are the authors referring here to aerosol composition, evolution of aerosol composition, gas aerosol phase partitioning, or something else? Arguably, the types and strengths of major sources for primary and secondary aerosol constituents are more important drivers of “the aerosol phase” than LWC and pH.

***Response**: Amended. The text now reads “Particle water (LWC) and pH are important characteristics of the aerosol phase, impacting on heterogeneous chemistry…”.*

See page 15, line 627 of the current file.

Page 29,526, lines 2-3. This statement is potentially misleading. Direct “in situ” measurement of pH in minimally diluted extracts of sampled aerosol can be reliably extrapolated to aerosol solution pHs at ambient LWCs [e.g., Keene et al., 2002, GRL; 2004, JGR]. The text should be clarified.

***Response**: The text has been rephrased **“**Direct measurements of aerosol pH “in situ” are challenging (e.g., Keene et al., 2002; 2004) and require careful considerations owing to the non-conserved nature of the hydronium ion and partial dissociation of inorganic and organic electrolytes in the aerosol. These challenges have led to the suggestion that indirect alternatives – such as measuring the semi-volatile partitioning of key species sensitive to pH, combined with comprehensive models may provide a reasonably accurate estimate of pH that can be carried out with routine measurements (Hennigan et al., 2015)…”.*

See page 17, lines 679-685 of the current file.

Page 29,526, lines 11-14. Hennigan et al. [2014] showed that reliable estimates of aerosol solution pH based on the thermodynamic properties of compounds with pH dependent solubilities require measurements of both gas- and particulate-phase concentrations. Model calculations based on “meticulous measurements” of aerosol composition alone do not yield reliable estimates of solution pH. The text should be clarified in this regard to minimize the potential for confusion.

***Response**: Indeed, Hennigan et al. (2015) show that we need in general to know gas and aerosol phase concentrations for an accurate and unbiased pH calculation. However, if some uncertainty or a known level of pH bias can be tolerated, aerosol measurements alone can still be quite informative for determining the pH. This was demonstrated quite well in Guo et al. (2015) and is also the case here; we will make sure all these points are emphasized and clarified in the manuscript. See also our relevant reply to the first general comment of the reviewer.*

See page 17, lines 696-699 of the current file.

Page 29,526, line 15. Most pH-dependent pathways involving the bioavailability of nutrients do not involve “catalytic” reactions. Suggest revising for clarity.

***Response:** Amended. The sentence now reads “Directly linked to aerosol pH and LWC is the bioavailability of nutrients contained within dust, involving pH-dependent catalyzed redox-reaction pathways”.*

See page 18, lines 700-701 of the current file.

Page 29,526, last 3 lines. The relative importance of different pathways for SO_2 oxidation is strongly pH dependent. The solubility of SO_2 in aerosol solutions at pH less than 3 is quite low and, consequently, in the presence acidic aerosol in this pH range, most SO_2 is oxidized in the gas phase [e.g., Keene et al., 1999, J. Aerosol Sci.] not via “heterogeneous” pathways as suggested by the authors. The text should be clarified.

***Response**: The statement was within the context of cloudy atmospheres and the presence of coarse mode dust particles. For clarification, the sentence now reads “…and the subsequent acidification through* *heterogeneous oxidation of the SO_2 on deliquescent dust particles within the plume, Meskhidze et al. (2003) concluded that…".*

See page 18, lines 713-715 of the current file.

Page 29,528, lines 8-16. Reliable estimation of LWC based on this approach requires that both nephelometers yield accurate results. Were the two instruments intercompared at the same RH to verify that results were directly comparable? The authors' approach also requires that particles pass at 100% efficiency through the drier. Was the passing efficiency of the dryer tested to verify that there were no significant line losses (e.g., to walls via electrostatic effects at low RH)? Finally, this approach requires that RH of 35% represents a reasonable threshold below which all aerosols effloresced. Was this verified via measurements at lower RH? Engelhart et al. [2011, ACP] report that aerosols at the Finokalia station can retain significant liquid water at RHs well below 35%. It would be helpful to report additional details regarding quality assurance procedures that were employed for this component of that analysis or, if the above issues were not addressed experimentally, to state and justify the associated assumptions that were required.

***Response**: Since 2011 the Finokalia station has been part of the European Research Infrastructure for the observation of Aerosol, Clouds, and Trace gases (ACTRIS) (http://actris.eu/). Being part of ACTRIS requires that all participants fulfill certain requirements and comply with Standard Operating Procedures in order to ensure the quality of data reported to the EBAS database. Therefore, both nephelometers are sent once a year for intercomparison at the World Calibration Centre (WCC) for Physical Aerosol Properties at the Leibniz Institute for Tropospheric Research in Leipzig, Germany. Intercomparisons are performed with the operating dryers. The same instruments and configurations have also taken part in other measurement campaigns in the past e.g. Kalivitis et al., 2011; Pilinis et al., 2014. Based on the ISORROPIA model run for metastable ammonium sulfate aerosol at an RH of 30%, the maximum water which can be contained under these conditions is 1.21 $\mu g\ m^{-3}$, which is less than 12% of the total submicron aerosol mass. Finally, Guo et al. (2015) have demonstrated that any small amount of water that may be present in low RH, does not necessarily correspond to a high LWC bias, because the water uptake increases exponentially with RH.*

See page 19, lines 753-755 and 759-760 of the current file.

Page 29,528, lines 17-19. It would be appropriate to specify the non-refractory constituents that were quantified by the ACMS and to report the associated detection limits. Since concurrent PM1 ionic compositions based on filter samples were measured in parallel, it would also be appropriate to mention the range in mass of refractory ionic constituents that were not characterized by the ACMS.

***Response**: We thank the reviewer for this comment. Constituents quantified by the ACSM include organics, sulfate, ammonium, nitrate and chloride. Detection limits for all constituents for 30 min of averaging time are provided in detail in the publication of Ng et al. (2011) and are for ammonium, organics, sulfate, nitrate, and chloride are 0.284 $\mu g\ m^{-3}$, 0.148 $\mu g\ m^{-3}$, 0.024 $\mu g\ m^{-3}$, 0.012 $\mu g\ m^{-3}$, and 0.011 $\mu g\ m^{-3}$, respectively. Bougiatioti et al. (2014) provide a comparison between ACSM and PM_1 filter values for sulfate, ammonium and organics as well as mass from ACSM constituents + Black Carbon compared to SMPS measurements, for a large subset (16/08-30/09/2012) of the sampling period of the current dataset. This is now referred to in the revised manuscript.*

See page 20, lines 770-777 and page 22, lines 841-846 of the current file.

Page 29,528, lines 22-23. It would be helpful to specify the size cut of the critical aperture in the ACMS. Is it precisely 1µm ambient diameter and, if not, what are the implications for comparison with results based on the PM1 filter samples?

***Response**: The aerodynamic lens of the ACSM allows for the detection of particles up to 700 nm. For the main aerosol constituents, i.e. organics, sulfate and ammonium, the results between the comparison of the ACSM and PM_1 filter concentrations is provided by Bougiatioti et al. (2014) and will be referenced in the text.*

See page 20, lines 777-782 of the current file.

Page 29,528, lines 28-28. The source for the “recommended collection efficiency” should be cited. It would also be appropriate to specify the constituents that were “verified by comparison” with the PM1 filter data, the number of paired observations that were compared, and the results of the comparisons (e.g., slopes, intercepts, and correlation coefficients for regressions of paired data).

***Response**: Amended, both source of the recommenced collection efficiency as well as the results of the comparisons with PM_1 filter data are cited in the revised manuscript, as a reference from Bougiatioti et al. (2014) supplementary material, which is a large subset of the currently presented data.*

See page 20, lines 775 and 777-782 of the current file.

Page 29,530, lines 18-19. It would be helpful to briefly address the range in magnitude of bias in the estimated mass introduced by ignoring refractory components other than BC (such as NaCl and non-ionic crustal constituents that are not quantified by the ACMS).

***Response**: Based on the study by Koulouri et al. (2008) for a two-year period at the same sampling site, it has been demonstrated that for fine particles (in that case $D_a<1.3$ μm) the contribution of the marine factor to the total loadings was 10.2%. Similarly, dust contribution in the fine fraction can vary between 6 and 10% for summer and winter, respectively. Nevertheless, during the sampling period presented in the manuscript, as already mentioned, the masses derived from ACSM+BC observations and from SMPS observations are in very good agreement, therefore the bias introduced by ignoring refractory components other than BC is regarded as minimum.*

See page 20, lines 786-791 and page 22, lines 842-846 of the current file.

Page 29,532, first few lines. The methods used to collect and analyze the PM1 filter samples, the constituents that were measured, and the associated data quality should be reported in the methods section.

***Response**: Amended, a short description for the PM1 filters analysis by ion chromatography is added in the instrumentation section (Section 2.2).*

See page 20, lines 783-791 of the current file.

Page 29,533, lines 1-10. This approach is confusing. Reliable results based on ISORROPIA run in the “forward” mode require measurements of the total (gas + aerosol) concentrations of aerosol precursors in the air parcel. How can reliable model calculations be run in the forward mode when “gas-phase measurements of ammonia ($NH_{3(g)}$) were generally not available?”

Response: *This comment is related to the first general comment of the reviewer that has been addressed in our corresponding replies. Indeed the least uncertain pH estimates are provided when both aerosol and gas phase measurements are considered. However, the use of only aerosol-phase concentrations in the forward mode calculation can still result in useful pH calculations. A sensitivity test in order to prove this assumption is carried out by comparing (a) the reproducibility of partitioning of inorganic semi-volatiles and (b) the shifts in calculated pHs by combining aerosol composition data with climatological values of gas-phase species.*

In addition, there is no mention of NH_3 measurements in the methods section. The measurement technique for NH_3, frequency of measurement, and data quality should be reported. How often were simultaneous measurements of NH_3 and NH_4^+ available?

Response*: This is a good point. A short description about the wet annular denuder (WAD) for the gas phase measurements along with the time resolution and uncertainty of the measurements is added in the instrumentation section.*

See page 21, lines 792-795 of the current file.

When the model was run in the "forward" mode for periods during which NH_3 was not measured (i.e., most of the time), it appears that NH_3 was initialized to 0.0 (i.e., NH_3 & NH_4^+ was assumed to equal to NH_4^+). This important point should be stated explicitly. Do the calculated pHs reported by the authors include those for periods when NH3 was available and considered in the calculations together with those for periods when NH_3 was not available and ignored in the calculations? If so, these results should be differentiated in some way since they are not directly comparable.

Response*: As $NH_{3(g)}$ measurements were not available for the whole period, calculation runs were indeed performed with NH_3 & NH_4^+ assumed to equal to NH_4^+. This is now explicitly stated in the revised version of the manuscript.*

See page 24, lines 898-899 of the current file.

As an alternative to estimating aerosol pH based on the phase partitioning of NH_3, if measured during the campaign, pH could also be estimated based on the phase partitioning of HNO_3 and/or HCl. Were gas-phase data available for either of these species?

Response*: The alternative proposed by the reviewer of estimating aerosol based on the phase partitioning of HNO_3 and/or HCl is not possible as the wet annular denuder (WAD) instrument was only connected to a cation chromatography system.*

The authors cite Guo et al. [2015] in support of the assumption that negative bias in calculated aerosol pH introduced by operating the model in the "forward" mode without NH3 data would be less than 1 pH unit (i.e., less than a factor of 10 in H^+ concentration). However, based on an assumed ratio of NH3 to NH4+, the cited analysis by Guo et al. (Section 4.2.5) actually suggests a somewhat greater upper limit for potential bias (1.38 pH units) and that upper limit excludes any additional uncertainty introduced by the assumed ratio of NH_3 to $NH4^+$. Consequently, the actual upper limit for bias based of Guo et al. [2015] would be greater than 1.38 pH units. Simple thermodynamic calculations over a range NH_3 mixing ratios reported in the literature also suggest that the likely upper limit for potential bias would be greater than 1.0 pH unit. In addition, results reported by Guo et al. correspond to the southeastern US, which represents a quite different chemical regime than that of the eastern coastal Mediterranean region so it is unclear that the potential magnitudes of inferred bias at the two locations are at all comparable.

***Response**: In order to see the direct influence of not including the gas phase ammonia measurements in the pH calculation, we performed a sensitivity study by adding different amounts of gas phase ammonia to the system and quantifying the response in pH. Initial results of ISORROPIA, the ones that are reported in the manuscript were compared to results obtained after adding 0.5, 1.2, 3.2 and 5* $\mu g\ m^{-3}$ *of ammonia. The values of 1.2 and 3.2* $\mu g\ m^{-3}$ *were the median and maximum values of the gas phase measurements respectively. These values are also within the observed values reported by Guo et al. (2015). A lower value (0.5* $\mu g\ m^{-3}$*) was also applied and finally 5* $\mu g\ m^{-3}$ *was selected as an extreme value which is very close to the European critical level for* NH_3*, established to 8* $\mu g\ m^{-3}$ *as an annual mean (Air Quality Guidelines for Europe, 2000). From a 3-year study conducted several years ago at the Finokalia station (Kouvarakis et al., 2001) it was seen that* $NH_{3(g)}$ *concentrations during summertime ranged from 0.02 to 1* $\mu g\ m^{-3}$ *with a mean and median value of 0.32 and 0.28* $\mu g\ m^{-3}$*, respectively, which is well below the maximum selected values for the sensitivity test. Therefore, based on climatology, neglecting the gas phase in the calculations has a difference of around 0.5 units in the pH (from 1.38 to 1.85 median values).*

The results of the sensitivity test are provided in the supplementary material (Figure S4) and below. Figure S4 shows the different pH median values with the 1st and 3rd percentile as derived for the different amounts of added ammonia. Error bars represent the upper and lower whiskers, derived from the 1st and 3rd percentile and the interquartile range (IQR). It can be seen that by adding even 5 $\mu g\ m^{-3}$ *of ammonia, pH values differ by a maximum of 1 unit (1.4 vs 2.4), as already mentioned in the manuscript. It can also be seen from both figures that between the addition of 3.2 and 5* $\mu g\ m^{-3}$ *of ammonia, the difference in pH is very small.*

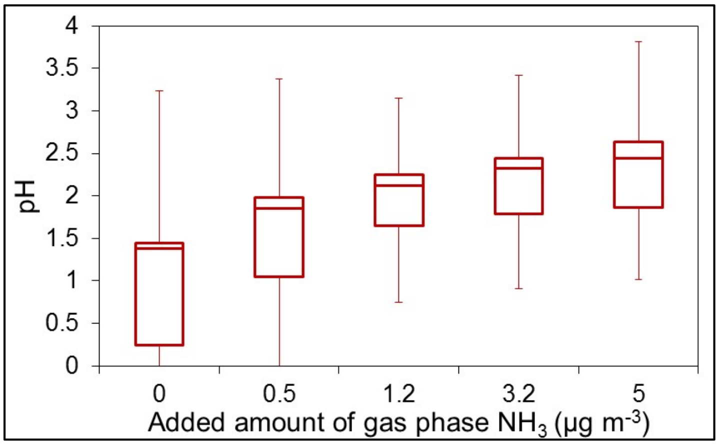

***Figure S4:** Box plot depicting the median pH values calculated by ISORROPIA II for the different amounts of added gas phase ammonia. Error bars represent the upper and lower whiskers (*Q_1*-1.5*IQR and* Q_3*+1.5*IQR, respectively).*

See Section 2.4, pages 24-25, lines 901-930 of the current file.

The authors could conduct a more credible error analysis by using their own data for the periods when NH_3 data were available to evaluate the potential range in bias under the ambient conditions that existed during the campaign. For those periods, they could simply compare results for "forward"-mode model calculations initialized with total NH_3 (NH_3 + NH_4^+) versus paired results for those initialized with only the corresponding NH_4^+.

***Response**: We thank the reviewer for this suggestion that we have followed, performed such error analysis and incorporated it in the revised manuscript. For the subset of the analyzed dataset when both NH_3 as well as ammonium from the ACSM data were available, we directly compared the pH and LWC valued derived from ISORROPIA in the forward mode when calculations were initiated with total (NH_3+NH_4^+) versus paired results (n=328) for the respective ones initiated with only particulate phase NH_4^+. The results show that for the specific periods, the addition of NH_3 in the calculations has a minimum effect to both pH (y=0.965x, R^2=0.584) and LWC (y=1.055x, R^2=0.993). This finding is now shown and discussed in the corresponding section (Section 2.4) of the revised manuscript.*

See page 25, lines 923-930 of the current file.

Based on the above, it appears that the inferred aerosol acidities reported by the authors are not representative or interpretable in terms of processes in the ambient atmosphere.

***Response**: In our earlier replies to the reviewer, we have addressed the issues raised by the reviewer concerning the reported aerosol acidities and we argued /shown that the computed pH values are representative of the fine fraction of aerosols while this is not the case for the coarse aerosols.*

Figure 1. It is virtually impossible to interpret some components of this figure. Suggest partitioning into multiple panels with different scales or converting to a stacked format with all constituents on the same scale. When available, it would also be helpful depict the NH_3 data.

***Response**: We agree with the reviewer that the readability of Figure 1 is not satisfactory. All reported data are for the period between June 8th and November 6th 2012. This will also be amended in the Methods section for the manuscript. Figure 1 will be converted to stacked format as proposed by the reviewer.*

See page 41 of the current file.

Figure 2. This figure would be easier to read if converted to a stacked format on the same scale. Lines connecting the time series during breaks in sampling should be removed as they were in Figure 1. To facilitate direct comparison, it would also help to use identical X axes on Figures 1 and 2. Many of the data depicted in Figure 2 precede the start of the campaign noted in the Methods section (August). Do data depicted in other figures correspond to the time series depicted in Figure 1 or in Figure 2? Unless otherwise specified, all information reported in the manuscript should correspond to the same period. Is there some reason why the earlier period of record was excluded?

***Response**: We thank the reviewer for pointing this out. The inconsistency of the time series between Figures 1 and 2 is now addressed and all information reported in the manuscript corresponds to the same period (June 8th to November 6th 2012). Both Figures 1 and 2 are now converted to a stacked format to the same scale.*

See page 42 of the current file.

Page 29,536, line 15, page 29,537, lines 12 to 21, Page 29,538, lines 9-16, and elsewhere. The method used to calculate trajectories, identify "the geographical sector and/or source region," and to characterize "...air masses influenced by mineral dust and by biomass burning" should be described in the methods section. For example, what specific criteria were used to define dust events (page 29,538) based on "... large amounts of particulate matter and high concentrations of crustal ions ...".

On page 29,539, the authors state that only "weak" dust events were sampled so it's unclear how the relative "amounts of particulate matter" allowed these "weak" events to be differentiated from periods with relatively less dust. In addition, Ca^{2+} originates from both marine and crustal sources. The method used to differentiate the "crustal" contribution should be specified in the methods section. Since non-sea-salt concentrations of Ca^{2+} at marine-influenced sites often correspond to small differences between relatively much larger numbers, the associated uncertainties can be proportionately quite large and should also be reported and considered in the context of employing Ca^{2+} as a crustal tracer. A figure with a map depicting the trajectories, source regions, and/or transport probability fields for the categories listed in Table 1 would also be a useful addition.

***Response**: The model and the conditions used for the calculation of the back trajectories are now described in the methodology section. The specific criteria based on crustal ions are also described and the methodology of the ion chromatography is also added. "Weak" dust events refer to PM_{10} concentrations not exceeding 55 $\mu g\ m^{-3}$. Crustal calcium is calculated by subtracting the concentrations of sea-salt Ca^{2+} = [Na]*0.038 and dust concentration can be estimated from nss-Ca^{2+}. This methodology has been used successfully for mass closure studies at the site (Sciare et al., 2005) and this information has been added in the methodology section. From the back trajectory analysis, a representative plot for each category type listed in Table 1 has been added in the supplementary material.*

See page 20, lines 785-786 and page 21, lines 817-819 of the current file.

Page 29,537, line 2, Table 1, and elsewhere. Presumably, the reported "average…pH" and associated standard deviation correspond to the average and standard deviation for aqueous concentrations of H^+ expressed as pH. If so, the text should be clarified. If not, both the results and the corresponding text should be revised accordingly. It is inappropriate to directly average lognormally distributed values such as pH.

***Response**: We kindly disagree here. Of course averaging of a non-linear metric, such as pH, would result in a biased value if we are considering mixing of samples into one volume that is allowed to react. Here, however, we are talking about temporal variability in aerosol properties; each time instant is independent from each other so averaging is acceptable.*

Page 29,538, lines 6 to 8. If retained, the methods used to collect and analyze the PM10 filter samples and the associated data quality should be reported in the methods section. However, when chemically distinct aerosol size fractions of PM10 are sampled in bulk, the pH of the bulk mixture differs from that of (1) the relatively less acidic supermicron size fractions with which HNO_3 and HCl partition preferentially and (2) the more highly acidic submicron size fractions with which NH_3 partitions preferentially. Consequently, based on both observations and theory, it is evident that sampling PM10 aerosol in bulk drives artifact phase changes of compounds with pH-dependent solubilities and, thus, pHs inferred from such bulk data are not representative. Chemically conservative constituents of PM1 and PM10 samples can be reliably compared and interpreted but ionic constituents of compounds with pH-dependent solubilities (including H^+, NO_3^-, Cl^-, and NH_4^+) cannot. The text and Table 1 should be revised accordingly.

***Response**: Once more we would like to point out the fact that the PM_{10} results are just indicative and not quantitative as obviously coarse particles are not in equilibrium with the gas phase. This will be emphasized in the revised manuscript. Nevertheless, the take-home message we wanted to point out with Table 1 is the prevalence of the fine or of the coarse fraction water and the pH values for the different types of sources/regions.*

See page 30, lines 1062-1068 of the current file.

Page 29,539, line 1. “nss” is not defined, the method used to calculate nss-K is not described, no nss-K data are reported, and nss-K is not an acid or a base and, thus, has no direct influence on the acidity or alkalinity of the aerosol.

***Response**: ‘Nss’ (Non-sea-salt) is now defined in the revised manuscript for clarity. Note however that the statement on nss-K is provided as an additional plausible reason found in the literature (Zhang et al. 2015 reference) why biomass burning aerosol exhibits higher pH values. It does not concern data from Finokalia station. No nss-K data are reported in our study, therefore no method to calculate nss-K is described. Non-sea-salt potassium (nss-K) is higher in air masses influenced by biomass burning (e.g. Zhang et al. 2015), and being an ionic species would partake in the pH calculations.*

See page 30, lines 1086-1088 of the current file.

Page 29,539, line 23. Suggest adding a citation to support the statement that the eastern Mediterranean in “P limited.”

***Response**: Good point. Done.*

See page 31, line 1109 of the current file.

Page 29,539, line 27. These results should be reported as “unpublished data” not cited as a manuscript in preparation.

***Response**: Done.*

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Particle water and pH in the Eastern Mediterranean: Sources variability and implications for nutrients availability.

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Abstract

Particle water (LWC) and aerosol pH are important parameters of the aerosol phase, affecting ~~drive the aerosol phase,~~ heterogeneous chemistry and bioavailability of nutrients that profoundly impact cloud formation, atmospheric composition and atmospheric fluxes of nutrients to ecosystems. Few measurements of in-situ LWC and pH however exist in the published literature. Using concurrent measurements of aerosol chemical composition, cloud condensation nuclei activity and tandem light scattering coefficients, the particle water mass concentrations associated with the aerosol inorganic (W_{inorg}) and organic (W_{org}) components are determined for measurements conducted at the Finokalia atmospheric observation station in the eastern Mediterranean between August and November 2012. These data are interpreted using the ISORROPIA-II thermodynamic model to predict pH of aerosols originating from the various sources that influence air quality in the region. On average, closure between predicted aerosol water and that determined by comparison of ambient with dry light scattering coefficients was achieved to within 8% (slope=0.92, R^2=0.8,

n=5201 points). Based on the scattering measurements a parameterization is also derived, capable of reproducing the hygroscopic growth factor (*f(RH)*) within 15% of the measured values. The highest aerosol water concentrations are observed during nighttime, when relative humidity is highest and the collapse of the boundary layer increases the aerosol concentration. A significant diurnal variability is found for W_{org} with morning and afternoon average mass concentrations being 10-15 times lower than nighttime concentrations, thus rendering W_{inorg} the main form of particle water during daytime. The average value of total aerosol water was 2.19±1.75 μg m^{-3}, contributing on average up to 33% of the total submicron mass concentration. Average aerosol water associated with organics, W_{org}, was equal to 0.56±0.37 μg m^{-3}, thus organics contributed about 27.5% to the total aerosol water, mostly during early morning, late evening and nighttime hours.

The aerosol was found to be highly acidic with calculated aerosol pH varying from 0.5 to 2.8 throughout the study period. Biomass burning aerosol presented the highest values of pH in the submicron fraction and the lowest values in total water mass concentration. The low pH values observed in the submicron mode and independently of air masses origin could increase nutrient availability and especially P solubility, which is the nutrient limiting sea water productivity of the eastern Mediterranean.

1. Introduction

Atmospheric particles have the ability to absorb significant amounts of water, which profoundly affects their physical and chemical properties (Khlystov et al., 2005), and impacts on atmospheric processes and health. Ambient concentrations of aerosol liquid water are controlled by the aerosol chemical composition, relative humidity (RH) and temperature, as it is largely in chemical equilibrium with the surrounding water vapor. Liquid water is ubiquitous and exceeds the total aerosol dry mass by 2 to 3 times on a global scale (Liao and Seinfeld, 2005). Therefore, the aerosol liquid water content (LWC) increases the particle size, affecting the particle lifetime and scattering efficiency. LWC and its strong dependence on relative humidity (RH) are the most important contributors to aerosol direct radiative cooling by aerosols (Pilinis et al., 1995). Numerous modeling studies suggest that reactions in aerosol liquid water are an important pathway of secondary organic aerosol (SOA) formation (Carlton and Turpin, 2013; Myriokefalitakis et al., 2011), thus playing an important role in the overall aerosol chemical composition. Aerosol water also has profound impact on the aerosol phase state, being able to transform semi-solid and viscous particles into homogeneous phase that are in equilibrium with their environment (Pöschl and Shiraiwa, 2015). This affects the timescale of heterogeneous reactions and ice nucleation. Nevertheless, despite the abundance and importance of LWC, it is not routinely measured, actual mass concentrations are uncertain, especially in the presence of organic compounds and model predictions of the property are often not evaluated (Nguyen et al., 2014).

Apart from the LWC, the pH of aqueous aerosols is another critically important aerosol property that drives many processes related to the aerosol chemical composition and gas-aerosol partitioning (Guo et al., 2015; Surratt et al., 2007; 2010; Meskhidze et al., 2003; Eddingsaas et al., 2010; Myriokefalitakis et al., 2015). Direct measurements of aerosol pH "in situ" are scarce (e.g., Keene et al., 2002; 2004) and require careful considerations owing to the non-conserved nature of the hydronium ion and partial dissociation of inorganic and organic electrolytes in the aerosol. These challenges have led to the suggestion that indirect alternatives – such as measuring the semi-volatile partitioning of key species sensitive to pH, combined with comprehensive models may provide a reasonably accurate estimate of pH that can be carried out with routine measurements (Hennigan et al., 2015). ~~A direct measurement of aerosol pH *in-situ* is not possible; instead indirect proxies are commonly used to represent the particle acidity (Guo et al., 2015; Hennigan et al., 2015).~~ The most frequently used proxy is the "ion balance", where the charge balance of measurable anions and cations is calculated, with the exception of the hydronium and hydroxyl ions; a surplus of cations implies an alkaline aerosol and vice versa. Often it is implied that a larger value of the ion balance implies a stronger acidity/alkalinity. As shown by Hennigan et al. (2015) and Guo et al. (2015), the ion balance (and other similar proxies discussed in Hennigan et al., 2015) fail in general to represent the true aerosol pH; only meticulous measurement of semi-volatile species (such as ammonia/ammonium) and other aerosol chemical constituents, combined with appropriate thermodynamic calculations (e.g. with ISORROPIA-II; Fountoukis and Nenes, 2007) are able to realistically provide particle pH and LWC (Hennigan et al., 2015). For an accurate and unbiased pH calculation both gas and aerosol phase concentrations are needed, however, when some uncertainty can be tolerated or the level of pH bias is known, aerosol measurements alone can still be quite informative for determining the pH, as demonstrated by Guo et al. (2015).

Directly linked to aerosol pH and LWC is the bioavailability of nutrients contained within dust, involving pH-dependent catalyzed redox-reaction pathways~~Directly linked to aerosol pH and LWC is the catalytic role of aerosol acidification on the bioavailability of nutrients contained within dust~~; upon deposition, increased availability of these nutrients may promote primary productivity in continental and marine ecosystems (e.g., Meskhidze et al., 2003; Nenes et al., 2011; Mahowald et al., 2008; 2009; Krishnamurthy et al., 2010). Acids (such as sulfuric and nitric) generated in the atmosphere from a variety of anthropogenic and biogenic sources, when mixed with mineral aerosols in sufficient amounts could lower the aerosol pH to values that increase the solubilities of Fe and P-containing minerals by several orders of magnitude (Stumm and Morgan, 1996; Shi et al., 2012). Nenes et al. (2011) have demonstrated that acidification can release considerable amounts of soluble phosphorus from soil-laden minerals (e.g., 81-96% of the total P found in Saharan dust and soil). Apart from P, the transport and deposition of mineral dust is believed to be a major, if not the dominant source of Fe to the remote ocean (Jickells et al., 2005). ~~With the incorporation~~ Considering the mixing of SO_2 ~~in~~ with advected dust plumes~~,~~ and the subsequent acidification through heterogeneous oxidation of the SO_2 on deliquescent dust particles within the plume, ~~and the subsequent acidification through heterogeneous oxidation~~, Meskhidze et al. (2003) concluded that ~~in~~ for aerosol with pH <2, 1-2% of the contained Fe would be mobilized within 3-5 days. Meskhidze et al., (2005) also demonstrated that sufficient acidification of Asian dust plumes could drive, upon deposition, a phytoplankton bloom in High Nitrate Low Chlorophyll regions of the North Atlantic. Solmon et al. (2009) also showed that simulated enhancements in particulate soluble iron driven by the chemical dissolution mechanism, can range from 0.5 to 6%, which is consistent with observations over the North Pacific Ocean.

The Eastern Mediterranean, being at the nexus of three continents (Europe, Asia and Africa), receives air masses influenced by a spectrum of human (traffic, biomass burning and industry) and natural (dust and marine) sources. It is therefore an ideal location to study atmospheric acidification of aerosols; very few studies however to date have accomplished that.

This study uses aerosol chemical composition measurements in conjunction with cloud condensation nuclei (CCN) concentration and light scattering coefficient (σ_{sp}) measurements to model the water mass concentrations (LWC) of aerosols from various sources in the Eastern Mediterranean. These data are then used in combination with the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007) to predict the aerosol pH for air masses that influenced air quality in the Eastern Mediterranean during the late summer and fall months of 2012.

2. Instrumentation and Methods

2.1 Measurement site

Aerosol measurements were conducted at the Finokalia atmospheric observation station in Crete, Greece (35°20'N, 25°40'E, 250m a.s.l.) between August and November 2012. The site (http://finokalia.chemistry.uoc.gr/) is a European supersite for atmospheric aerosol research and is part of the ACTRIS Network (Aerosols, Clouds, and Trace gases Research Infrastructure) (http://www.actris.eu/). The station is located at the northeastern part of the island of Crete, facing the Mediterranean Sea covering the whole northern sector. Being away from direct urban influence, the station is representative for background measurements in the Eastern Mediterranean and sampled air masses arriving at the site have most commonly a marine source region or originate from continental Europe and Greek mainland. Moreover, dust events from Northern Africa (Sahara) occur often during spring and autumn. More details for the Finokalia station and the prevailing climatology in the area are given by Mihalopoulos et al. (1997).

2.2 Instrumentation and Methodology

PM_1 (Particulate Matter of diameter smaller than 1 μm) aerosol light scattering coefficients (σ_{sp}) were measured online with the use of two different nephelometers to infer the LWC. Particle dry scattering was measured with a 3-wavelength Aurora 1000 Integrating Nephelometer, located in an air-conditioned sampling trailer and operated with a diffusional silica dryer upstream, which maintained the RH below 35%. Based on the ISORROPIA model run for metastable ammonium sulfate aerosol at an RH of 30%, the maximum water which can be contained under these conditions is 1.21 μg m^{-3}, which is less than 12% of the total submicron aerosol mass. The nephelometer for the particle wet scattering was a Radiance Research M903, located outside the trailer in order to provide a scattering measurement at ambient T and RH. This second nephelometer was equipped with a VAISALA Inc. Humitter 50U Integrated Humidity and Temperature probe in order to record the ambient values of T and RH with an accuracy at 20 °C specified to be better than ±5% RH. Both nephelometers take part in yearly intercomparisons within the ACTRIS network.

The real-time, quantitative measurements of the non-refractory components of the submicron aerosol were provided by an Aerosol Research Inc. Aerosol Chemical Speciation Monitor (ACSM; Ng et al., 2011). Ambient air was draw into the ACSM by a multiple PM_{10} (Particulate Matter of diameter smaller than 10 μm) aerosol inlet operating at Finokalia, with a temporal resolution of 30 minutes. At the inlet of the ACSM and via a critical aperture mounted at the entrance of an aerodynamic lens, the submicron fraction of the aerosol is sampled. The aerodynamic lens of the ACSM allows for the detection of particles up to 700 nm diameter. The focused particle beam is then transmitted through two vacuum chambers and into a detection chamber where the particles impact on a hot plate and flash vaporized. Finally they are detected and characterized with the use of an electron impact quadrupole mass spectrometer. Constituents quantified by the ACSM include organics, sulfate, ammonium, nitrate and chloride. Detection limits for all constituents for 30 min of averaging time are provided by Ng et al. (2011) and are for ammonium, organics, sulfate, nitrate, and chloride are 0.284 μg m^{-3}, 0.148 μg m^{-3}, 0.024 μg m^{-3}, 0.012 μg m^{-3}, and 0.011 μg m^{-3}, respectively. Mass concentrations are calculated with the recommended collection efficiency of 0.5 for all constituents (Ng et al. 2011) and ~~are~~ the main aerosol constituents i.e. organics, sulfate and ammonium are verified by comparison with other concurrent measurements (daily PM_1 filters; ~~Stavroulas et al., 2015~~Bougiatioti et al. (2014) supplementary material). PM_1 filters (Pallflex Tissuquartz, 47 mm diameter) were collected using a built-in system comprised of the four upper stages (stage 8-11) of a low-pressure Berner impactor (PLBI; Berner and Lürzer, 1980). Furthermore, daily PM_{10} filters are also collected on site using a sequential sampler (Leckel, SEQ47/50). A detailed study of the comparison between ACSM and PM_1 filter values for a large subset of the present data (16/08-30/09/2012) is provided by Bougiatioti et al. (2014).

PM_1 and PM_{10} filters were analyzed by ion chromatography (IC) for anions (Cl^-, Br^-, NO_3^- (nitrate), SO_4^{-2} (sulfate), $C_2O_4^{-2}$ (oxalate)) and cations (K^+, Na^+, NH_4^+ , Mg^{2+}, Ca^{2+}) using the procedure described by Bardouki et al. (2003). From the calcium, the crustal component can be estimated by subtracting the contribution of sea-salt Ca^{2+} = [Na]*0.038 and dust concentration is estimated using the approach of Sciare et al. (2005). Based on the study by Koulouri et al. (2008) for a two-year period at the same sampling site, it has been demonstrated that for fine particles (in that case D_a<1.3 μm) the contribution of the marine source to the aerosol mass was 10%. Similarly, dust contribution in the fine fraction can vary between 6 and 10% for summer and winter, respectively.

From 25/6 to 7/8/2014, gas phase ammonia measurements were also conducted at Finokalia, using a wet annular denuder (WAD; Wyers et al., 1993; Spindler et al., 2003) coupled with an ion chromatography system (Dionex ICS-1500) quantifying cations with an hourly resolution in order to check the validity of our calculations in the absence of gaseous phase NH_3 (see section 2.4). Concurrent black carbon (BC) measurements were performed on site using a seven-wavelength aethalometer (Magee Scientific, AE31) with a time resolution of 5 min. Based on previous studies at Finokalia, BC is found mainly on the fine aerosol fraction (Koulouri et al., 2008; Bougiatioti et al., 2014) hence these values are used in addition to the ACSM concentrations to calculate the dry aerosol mass of the PM_1 fraction.

Size-selected cloud condensation nuclei (CCN) measurements were obtained using a Droplet Measurement Technologies, Continuous Flow Streamwise Thermal Gradient CCN counter (CFSTGC). Particles of 60, 80, 100 and 120 nm were first size-selected by a differential mobility analyzer (DMA), split into two and one of these flows was introduced in the CCN counter. The total number of condensation nuclei (CN) was measured by a condensation particle counter (CPC; TSI 1772) situated downstream the first DMA. In the CCN counter, the activated droplets are sized and counted by an optical particle counter (OPC) after exiting the growth chamber. The instrument was operated in scanning flow CCN analysis mode (SFCA; Moore and Nenes, 2009), where the flow rate in the growth chamber changes over time, while a constant temperature difference is maintained. In that way the supersaturation changes continuously, providing activation spectra with a high temporal resolution. The flow rate was increased linearly between a minimum and a maximum flow rate and sigmoidal activation curves of CCN vs flow rate were recorded, with the inflection point of the sigmoid representing a critical activation flow, Q_{50}, that corresponds to a critical supersaturation, $S*$, above which particles act as CCN. From the critical supersaturation and knowledge of the particle dry diameter, with the application of Köhler theory, the hygroscopicity parameter kappa (Petters and Kreidenweis, 2007) is obtained, which is then used to determine the LWC associated with organic components of the aerosol (Guo et al., 2015). Finally, analysis of 5-day back trajectories of air masses arriving at Finokalia at 1000 and 3000 m above ground level every 6 h was conducted with the help of the HYSPLIT model (www.arl.noaa.gov /hysplit.php; Stein et al., 2015).

2.3 Determination of LWC from nephelometers

The particle water was inferred using the approach of Guo et al. (2015), where the ratio of the wet and dry PM$_1$ scattering coefficients (σ_{sp}) measured by the two nephelometers is used. For this, the aerosol hygroscopic growth factor ($f(RH)$) is calculated according to a well-established method based on the two scattering coefficients: $f(RH)=\sigma_{sp(wet)} / \sigma_{sp(dry)}$ (e.g. Sheridan, 2002; Magi, 2003; Kim et al., 2006). These scattering coefficients in ambient and dry conditions are proportional to the diameter of average surface $\overline{D_p}$ and the average scattering coefficients $\overline{Q_s}$, so that :

$$\overline{D_{p,ambient}} = \overline{D_{p,dry}} \sqrt{f(RH)\overline{Q_{s,dry}} / \overline{Q_{s,ambient}}} \qquad (1)$$

Assuming that the two average scattering efficiencies are almost equal, LWC is then equal to the difference between ambient and dry particle volume, and by substitution of the dry diameter of average surface:

$$\overline{D_{p,dry}}^3 = \frac{m_p}{\left(\frac{\pi}{6}\right)\rho_p N_t} \qquad (2)$$

where N_t is the total number concentration, ρ_p is the density of dry aerosol and m_p is the dry mass concentration, we arrive at the simplified expression of:

$$LWC = [f(RH)^{1.5} - 1]\frac{m}{\rho_p} \qquad (3)$$

The simplification assumption that the dry and ambient scattering efficiencies are almost equal introduces an error in the derived LWC, which based on the detailed analysis of Guo et al. (2015) is of the order of 10% at RH=76.4%, but can reach up to 21% at RH=90%.

For this set of measurements the PM$_1$ dry mass concentration is calculated from the sum of the ACSM constituents combined with the BC measurements. During the sampling period, the comparison between the sum of ACSM and BC masses and the submicron mass derived from a scanning mobility particle sizer (SMPS; TROPOS-type) is very good (y=0.96x, R^2=0.67 for a period of 2-years; Figure S3). Therefore the bias introduced by ignoring other refractory constituents than BC is minimal, which is in agreement with size-segregated aerosol chemical composition measurements already conducted at Finokalia (e.g. Koulouri et al., 2008). The particle density, ρ_p, was estimated from the particle composition from the ACSM ammonium, organics and sulfate, using an organic density of 1.35 g cm^{-3} as determined by Lee et al. (2010) for the same site during the summer of 2008, the density of ammonium sulfate (1.77 g cm^{-3}) and the equation:

$$\rho_p = \left[\frac{x_{a/s}}{\rho_{a/s}} + \frac{x_{org}}{\rho_{org}} \right]^{-1} \qquad (4)$$

where $x_{a/s}$ is the mass fraction of ammonium sulfate and x_{org} is the mass fraction of the organics, and $\rho_{a/s}$ and ρ_{org} are the densities of ammonium sulfate and the organics, respectively. It must be noted that nitrate is not taken into account as its concentrations are very close to the limit of detection of the ACSM for the PM_1 fraction at the Finokalia site during the studied period. Particle density was calculated to be 1.56±0.08 g cm^{-3} (n=6028), with aerosol concentration ranging from 1.33 to 16.65 μg m^{-3} and average value of 5.62±3 μg m^{-3}. The particle water calculated by this method is hereafter referred to as *f(RH)_*water, with the uncertainty of this calculation being estimated to be 23% (Guo et al., 2015).

2.4 LWC and pH prediction from chemical composition

The water vapor uptake by aerosol establishing equilibrium for ambient temperature and relative humidity conditions is influenced by both inorganic and organic components. LWC, therefore, is directly dependent on aerosol chemical composition and meteorological conditions, as well. As proposed by Guo et al. (2015) and explained below, we calculated the particle water associated with inorganics (W_{inorg}) and the particle water associated with organics (W_{org}). The sum of these two ($W_{inorg}+W_{org}$), equal to the total particle water, is then compared to the LWC determined by the two nephelometers.

First the particle pH was calculated by the thermodynamic model ISORROPIA-II for the PM_1 aerosol fraction. W_{inorg} was calculated based on a thermodynamic equilibrium between an inorganic aerosol (NH_4-SO_4-NO_3-Cl-Na-Ca-K-Mg-water) and its gas phase precursors. For the current analysis, the inputs to ISORROPIA-II are the inorganic ions measured by the ACSM with a 30 min time resolution (except for Cl which is at the detection limit of the instrument at the specific site), the average daily values for Na^+, Cl^-, Ca^{2+}, K^+ and Mg^{2+} determined by ion chromatography analysis of PM_1 filters, and RH and T measured by the ambient nephelometer probe. The use of daily values for the macromineral elements obtained from the filter analysis could introduce potential artifacts in the calculation, but is believed to be limited as almost 90% of the fine fraction mass in the area can be attributed to ammonium sulfate and organics (Koulouri et al., 2008; Bougiatioti et al., 2009;2013).

The contribution of the organic components to particle water (W_{org}) was determined from the organic hygroscopicity parameter (κ_{org}) from the observed CCN activities of the organic fraction (Cerully et al., 2014):

$$W_{org} = \frac{m_s}{\rho_s} \frac{\kappa_{org}}{\left(\frac{1}{RH} - 1 \right)} \qquad (5)$$

where m_s and ρ_s are the organic mass concentration from the ACSM and an organic density, respectively determined as described in section 2.3.

Finally, the particle pH is calculated by the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) based on the calculated equilibrium particle hydronium ion concentration in the aerosol. As ISORROPIA-II does not take into account the LWC associated with the organic aerosol, a recalculation of pH is made by considering the predicted particle hydronium ion concentration per volume of air (H^+_{air}) and the total predicted water ($W_{inorg}+W_{org}$) (Guo et al., 2015):

$$pH = -\log_{10} H^+_{aq} = -\log \frac{1000 H^+_{air}}{W_{inorg} + W_{org}} \qquad (6)$$

where the modeled concentrations for LWC and H^+_{air} are µg m^{-3}, and H^+_{aq} (mol L^{-1}) is the hydronium concentration in an aqueous solution and W_{inorg} and W_{org} are in µg m^{-3}. ISORROPIA-II has been previously tested and was able to predict the equilibrium partitioning of ammonia and nitric acid to within measurement uncertainty (Nowak et al., 2006; Fountoukis et al., 2009; Hennigan et al., 2015; Guo et al., 2015). Here, ISORROPIA-II was run in the "forward mode" assuming a metastable aerosol state. It should be noted that gas phase measurements of ammonia ($NH_{3(g)}$) were generally not available for the whole measurement period and the sum of NH_3 and NH_4^+ is assumed to be equal to NH_4^+. Therefore it is expected that the pH ~~to~~ could be underpredicted by at most one unit (Guo et al., 2015; Weber et al., 2016).

To assess the uncertainty in our calculations by not including gas phase NH_3, a sensitivity analysis is performed by adding different amounts of $NH_{3(g)}$ to the system and quantifying the response in pH. Initial results of ISORROPIA, were compared to results obtained after adding 0.5, 1.2, 3.2 and 5 µg m^{-3} of ammonia. The values of 1.2 and 3.2 µg m^{-3} were the median and maximum values of the gas phase measurements conducted with the WAD during summer 2014, respectively. These values are also within the observed values reported by Guo et al. (2015). A 3-year study conducted at the Finokalia station (Kouvarakis et al., 2001) reported that NH$_{3(g)}$ concentrations during summertime have an average of 0.27 μg m^{-3} (range from 0.07 to 0.68 μg m^{-3}). Thus, a lower value (0.5 μg m^{-3}) to represent these measurements was also applied and finally 5 μg m^{-3} was selected as an extreme value which is very close to the European critical level for NH$_3$, established to 8 μg m^{-3} as an annual mean (Air Quality Guidelines for Europe, 2000). The results of the sensitivity study are provided in detail in the supplementary material and clearly show that neglecting the gas phase NH$_3$ in the calculations leads to an underestimate of around 0.5 units in the pH (from 1.38 to 1.85 median values) for the NH$_3$ range reported for Finokalia.

The above results are further supported by the partitioning of nitric acid between the condensed (NO$_3^-$) and gas phase (HNO$_3$). Assuming ideal solutions for the average conditions during the study period derived from ISORROPIA-II, it is calculated that little nitrate should be present in the aerosol phase when pH is lower than 3 (Figure S5 Supplementary). Indeed, with an average concentration of nitrates of 0.12±0.06 μg m^{-3} in the fine mode and the resulting partitioning coefficient of less than 0.2, it is derived that the maximum value of pH that can be observed for the current conditions is 2. This value is in total accordance with the upper limit of pH of 1.85 derived from the formerly presented sensitivity analysis.

For days where NH$_{3(g)}$ measurements exist (summer 2014), following the same methodology as before, the measured concentrations of NH$_{3(g)}$ and predictions by the model are in fairly good agreement. Observed gas phase concentrations have an of 0.79±0.27 μg m^{-3} while predicted concentrations have an average of 0.65±0.32 μg m^{-3}. Additionally, we directly compared the pH and LWC values derived from ISORROPIA in the forward mode when calculations were initiated with total (NH$_3$+NH$_4^+$) versus paired results (n=328) for the respective ones initiated with only particulate phase NH$_4^+$. The results show that for the specific periods, the addition of NH$_3$ in the calculations has a minor effect to both pH (y=0.965x, R^2=0.584) and LWC (y=1.055x, R^2=0.993).

~~*This* also implies that the computed vapor pressure of NH$_{3(g)}$ will be underestimated, as the total ammonia/ammonium is not known to be introduced to the model However, for the days that available data of NH$_{3(g)}$ do exist, measured concentrations and predictions by the model are in fairly good agreement: Gas phase measurements have an average concentration of 0.79±0.27 μg m^{-3} while predicted concentrations have an average of 0.65±0.32 μg m^{-3}.~~

3. Results and Discussion

3.1 PM$_1$ chemical composition and f(RH)_water

For the measurement period, the average values for the main aerosol constituents were 1.85±0.94, 2.31±1.61, 0.81±0.58 and 0.52±0.22 μg m^{-3} for organics, sulfate, ammonium and BC, respectively. In terms of contribution to the PM$_1$ mass concentration, the two most abundant components of the submicron range were sulfate and organics, with mass fractions of 39.6 and 33.8% respectively, followed by ammonium (14.8%), BC (9.3%) and nitrate (2.1%). Chloride has a negligible contribution to the total submicron mass concentration. The time series of the main aerosol constituents and their overall contribution, as measured by the ACSM, are portrayed in Figure 1. Nevertheless, a fluctuation of 10-20% in sulfate and/or ammonium concentrations is not expected to be reflected in a pH change, given the logarithmic scale of the property, which is consistent with the findings of Weber et al. (2016) that pH has a weak sensitivity to a wide range of SO_4^{2-} and NH_3. This is further elaborated by the sensitivity analysis of gas phase ammonia, where the 5-fold increase of added amount of NH_3 causes a unit change in pH, on average. More details about the ACSM measurements and performance can be found in Stavroulas et al. (~~2015~~in preparation, 2016).

The chemical composition is expected to influence the water content of aerosol, as well. Mean *RH* and *T* during the study period were 57±11% and 27.4±3.7 °C. As described in the section 2.3, *f(RH)*_water was calculated from the data from the two nephelometers. With the use of equations 1 and 2, we calculated LWC from the nephelometers for the whole measurement period. The average value of *f(RH)*_water was 2.19±1.75 μg m^{-3}, which according to the dry mass measurements, can contribute on average, up to 33% of the total submicron mass concentration. We also sought to establish a link between *f(RH)* and *RH* and taking into account all available scattering data (n=7044) the following parameterization has been established:

$$f(RH) = 1.067(\pm 0.004) + 1.99(\pm 1.05)\cdot 10^{-7}\, RH^{3.547(\pm 0.035)} \qquad (7)$$

Based on this, we reconstructed the time series of the hygroscopic growth factors, with a very good correlation between calculated and measured values (y=0.99x, R^2=0.85) (also see Supplementary Material). This parameterization does not appear to be influenced by changes in the chemical composition. Uncertainties in the RH measurement by the probe are in the order of 5% while dry and wet aerosol light scattering coefficients measurement uncertainty is in the order of 20%.

3.2 Inorganic and organic water predictions

3.2.1 Inorganic aerosol water

The thermodynamic model ISORROPIA-II (http://isorropia.eas.gatech.edu; Fountoukis and Nenes, 2007) was used to predict the contribution of inorganic species to LWC. The water attributed to the inorganic component of the aerosol has an average value of 1.77±1.45 μg m^{-3}. The lowest values are observed during August, probably because of the higher temperatures that enhance evaporation of water from the aerosol. The timeseries for aerosol water associated both with inorganic and organic aerosol components are shown in Figure 2, where it can be seen that most of the time, the variability of the two water components follow each other closely, with water concentrations associated with organics being about 1:10 (12±9%) of those associated with the inorganic aerosol components.

3.2.2 Organics: hygroscopicity and aerosol water

The contribution of the organic submicron fraction of the aerosol to the particle water was calculated from the combination of the CCN and chemical composition measurements, as described in section 2.4. Assuming that the cumulative aerosol hygroscopicity can be represented as the sum of contribution of the inorganic (expressed mostly by ammonium sulfate) and organic fraction of the aerosol, the measured hygroscopicity can be calculated by the sum:

$$\kappa = \varepsilon_{inorg}\kappa_{inorg} + \varepsilon_{org}\kappa_{org} \qquad (8)$$

where ε_j and κ_j are the volume fraction and hygroscopicity of the inorganic and organic species. Once the aerosol species concentrations are determined, the corresponding volume fractions for ammonium sulfate and organics are calculated, and a set of hygroscopicity parameter equations is produced. As mentioned in the section 2.2, hygroscopicity parameters for 60, 80, 100 and 120 nm particles are measured. In a former CCN study at the same site (Bougiatioti et al., 2011) it was shown that from many different particle sizes, the characteristic hygroscopicity parameter κ^* of the 100 nm particles was the closest one to the κ determined by PM_1 filter measurements. Therefore we created two different sets of kappa equations along with the volume fractions to calculate the total κ^*, one for the 100 and another one for the 120 nm. With the subsequent application of multivariate regression analysis to the set of n=2429 and 1801 equations (for 100 and 120 nm respectively), κ_{org} is determined to be 0.28±0.01 based on the $\kappa_{\_100nm}$ and 0.24±0.01 based on the $\kappa_{\_120nm}$. The average value of 0.26 is used in equation 5 to calculate the time series of W_{org}. The average value W_{org} was thus found to be 0.56±0.37 μg m^{-3}, which constitutes on average ~27.5% of the calculated *f(RH)*_water. The overall uncertainty of this calculation is estimated by Guo et al. (2015) to be around 30%. That study for south eastern United States of America, found a higher contribution of organic species (on average 35%) to the total water that can be explained by the dominance of organics in the submicron range aerosol, with an average mass fraction of 67%.

3.2.3. Aerosol water

Aerosol water is the sum of $W_{org}+W_{inorg}$, determined as previously explained. This can be further compared with the time series of the *f(RH)*_water deduced from concurrent observations by the two nephelometers (section 2.3), independent from the aerosol water calculated as here explained. The particle water predicted from the sum of the organic and inorganic contributions to the water agrees very well with the water measured by the nephelometers (Figure 3). More specifically, the total predicted water is highly correlated and on average within 10% of the measured water, with slope=0.92 and R^2=0.8 for the whole measurement period (n=5201 points).

The diurnal variability of the calculated water components, along with the total measured water, ambient T and RH is shown in Figure 4. It must be noted at this point that the presented diurnal variability corresponds to the entire period of the study and this pattern seems to be independent of the geographical sector and/or source region, based on the backtrajectory analysis. The diurnal variability of aerosols from different sources, further presented at Section 3.4, have been explicitly studied and found not to differ significantly, therefore the total diurnal variability was selected as being representative of the whole measurement period. Predicted and measured aerosol LWC diurnal variabilities are in very good agreement. As expected, the highest LWC values are observed during nighttime, when RH is also at its maximum, resulting in significant water uptake. W_{org} shows a significant diurnal variability with morning and afternoon average mass concentrations being 10-15 times lower than nighttime ones. Thus, during daytime W_{inorg} is the main component of particle water as the average values for the predicted water ($W_{org}+W_{inorg}$) are very close to the ones of the inorganic water alone. On the other hand, during nighttime, the two averages start to diverge and this could be attributed to the higher contribution of organic water during nighttime, when the photochemical activity and temperature are minimum and RH high.

3.3 Aerosol pH

The predicted pH for the aerosols collected at Finokalia during the studied period was highly acidic with an average value of 1.25±1.14 (median 1.51) and varying between -0.97 and 3.75. pH varied by almost 1 unit throughout the day. This can be translated as an almost 10-fold increase of the H^{+}_{air}/LWC ratio from early morning to mid-day and to a lesser extent during early night. This significant variation in pH can be partially explained by the diurnal variation of H^{+} and its increase which coincides temporally with the decrease in pH (Figure 5) and by the reduction of aerosol water (LWC) during daytime compared to the higher LWC during nighttime (Figure 4). This implies the diurnal variability of pH is mostly driven by the reduction of aerosol water during daytime compared to the higher aerosol water during nighttime.

When studying the diurnal variability of pH for the different sources/geographical sectors (supplementary material) it occurs that pH differs depending on the source and origin of the air masses. Air masses from the northwestern, northeastern Europe and Turkey, as well as from Greek mainland, do not exhibit significant diurnal variability. When no distinction is made between source regions, the pattern of the overall pH variability with a drop in pH values during midday as presented in Fig. 5, is similar to -the diurnal variability of pH for air masses influenced by mineral dust (coming from the SW) and by biomass burning, but with pH values from biomass burning being 1-1.5 units higher. Nevertheless, the mean pH values for each one of the source regions are very close to the overall pH mean value when no distinction of origin is made.

Furthermore, accounting only for the water associated with the inorganic aerosol component, particle water is underestimated by around 9%, thus resulting in a slightly lower pH (more acidic) by 0.07-0.38 units of pH (Figure 6a). As seen in section 3.2, W_{org} is on average 27.5% of the total water, as a result the pH increases by 0.14 units when the organic water is included (Figure 6a). When the contribution of organic water is taken into account, the recalculation of pH gives an average value of 1.38±1.11 (median 1.65). The pH calculated by ISORROPIA-II correlates very well with the pH corrected using equation 6 for inclusion of the organic water ($W_{org}+W_{inorg}$) (R^2=0.98, Figure 6b). Subsequently, if organic mass and organic hygroscopicity data are not available, ISORROPIA-II solely based on inorganic composition data, will provide an adequate estimate of both H^{+}_{air} and W_{inorg} and thus of pH.

3.4 Aerosol water and pH based on aerosol fraction and source region

Apart from the time-resolved aerosol water and pH calculations for the submicron aerosol fraction, aerosol water and pH were also calculated based on the daily PM$_{10}$ filter chemical composition analysis. It should be noted at this point that there is a strong link between aerosol pH and aerosol size distribution due to the chemical composition changes in the aerosol size. For PM$_1$ which is in equilibrium and chemical composition is determined by high time resolution measurements leads to higher accuracy in the pH calculations. On the other hand, as PM$_{10}$ particles are not in equilibrium, the respective acidity results are subject to biases and are less quantitative than the submicron results. For comparison purposes the corresponding PM$_1$ measurements, based on ACSM and the respective PM$_1$ ionic concentrations for cations such as Na$^+$, Ca^{2+}, Mg^{2+}, corresponding to the fine fraction, have also been averaged to daily values. Characteristic source regions/sources were subsequently selected based on back-trajectory analysis and chemical tracers. Furthermore, biomass burning events have been identified based on source apportionment of BC and Positive Matrix Factorization (PMF) analysis of the organic mass spectra obtained from the ACSM as detailed in Bougiatioti et al. (2014). Dust events were identified by backtrajectory analysis of the air masses, originating from Northwestern Africa and confirmed as by containing large amounts of particulate matter (45-55 μg m^{-3} in PM$_{10}$ mass) and high concentrations of crustal ions, such as Ca^{2+} (median concentration during dust events of 1.8 μg m^{-3} versus 0.6 μg m^{-3} for the rest of the days) . The main measured and calculated parameters are presented in Table 1.

It can be seen that, in general, for anthropogenic-laden air masses (e.g. from Istanbul, Black Sea and Continental Europe) aerosol mass resides mainly (60-70%) in the submicron aerosol and thus the submicron fraction seems also to drive the pH of PM$_{10}$, while most of the aerosol water (~70%) is present in the coarse fraction. Biomass burning exhibits the highest values of pH in the submicron fraction and the lowest values in total water mass concentration. Interestingly enough, the value of 2.77 for biomass burning pH is well above the value of 2, which favors the partitioning of nitrate to the aerosol phase (e.g., Meskhidze et al., 2003) The correlation observed during fire events between biomass burning organic aerosol and particulate nitrates (e.g. Bougiatioti et al., 2014) may be explained by these higher pH levels, rather than just high levels of nitric acid and/or ammonia. As found in the literature, h~~H~~igher pH levels of biomass burning aerosol can also be attributed to higher concentrations of ~~nss-K~~non-sea salt potassium, which as an ionic species influences pH (Zhang et al. 2015), rendering aerosol more alkaline. Based on the calculated ratios for pH and particle water, it can be derived that the ions that set the bulk pH is mostly driven by the fine mode; the LWC however is associated mostly with the supermicron aerosol mass. Hygroscopic sea salt components are also found in the coarse mode, which can justify the larger contribution of PM_{10} total water, while the submicron fraction may be composed mostly of less hygroscopic, organic components (Bougiatioti et al., 2015). Even though strong dust events were lacking during the study period, numerous weaker events were captured. From these events it occurs that aerosol mass, total water and pH are mostly driven by the coarse aerosol fraction. This is consistent with the findings of Koulouri et al. (2008) that most (86%) of the mass of crustal components were found in coarse particles. In terms of mass concentration, the two natural sources, namely air masses of marine and dust origin, contain the largest amounts of total submicron water. Even though total water exhibits the highest mass concentrations for the specific sources, the relative contribution of organic water to the submicron fraction is the lowest (16% for dust and 17% for marine, based on the median values). For the two natural sources, the ratio between submicron pH and calculated pH for the PM_{10} fraction is the lowest observed (Table 1), namely 30±17% (median 25%) and 6±19% (median 5%).

3.5 Atmospheric implications

The pH values for submicron and PM_{10} fractions is also expected to affect many processes, such as the solubility and therefore the bioavailability of nutrients and especially phosphorus (P) and iron (Fe). This is of crucial importance for seas such as the eastern Mediterranean for which primary productivity is P limited (Krom et al., 1991). One of the striking results of the aerosol pH calculations (presented in Table 1) is that with the exception of biomass burning, pH of all submicronic aerosols including those originating from desert dust is highly acidic with values typically below 2. Although the nutrient flux from the fine mode is certainly smaller than in the coarse mode, it can be transported much further away from source regions before deposition, and be considerably more acidified (hence bioavailable). Based on published literature (Nenes et al., 2011; Meskhidze et al., 2003) under acidic conditions similar to the derived pH aerosol values, the acid-mobilized dissolution of such nutrients is expected to be of great importance. ~~dust dissolution experiments performed in our laboratory (Nikolaou et al., under preparation), under acidic conditions similar to the derived pH aerosol values, the solubility of P and Fe has been found to be equal to 32% and 9%, respectively. These percentages vary slightly depending on dust~~

~~concentration and are almost 3 and more than 10 times higher than those observed under neutral pH or seawater pH conditions, respectively, and imply significant influence of aerosol pH on nutrients release even for desert aerosols.~~

Markaki et al. (2003), by analyzing PM_{10} aerosols collected in Greece (Finokalia) and Turkey (Erdemli) for dissolved inorganic (DIP) and Total (TP) phosphorus levels have shown that although the SW sector, corresponding to the Sahara, presented TIP levels by a factor of two higher than the European (NE or NW) sectors, the lowest values for the DIP/TIP ratio are associated with the SE and SW sectors, and the highest with the N sectors (difference of almost a factor of 2). The explanation for that behavior is given by the ratio of pH in PM_1 and PM_{10} aerosols that is presented in Table 1. In aerosols from the NW sector only a very small difference in pH between the two fractions is observed, while in desert aerosols the large amount of dust present in the coarse mode highly influences pH of PM_{10} leading to a significant decrease of acidity and thus P solubility. However as dust events can transport large amounts of P (up to a factor of three higher than in air masses coming from Europe), any future change in PM_1/PM_{10} ratio caused by dust events will significantly influence P availability and deposition to the eastern Mediterranean sea and thus to its productivity.

Conclusion

Using the aerosol chemical composition measurements by ACSM, thermodynamic models, such as ISORROPIA-II, and CCN measurements we calculated the particle water associated with both inorganics (W_{inorg}) and organics (W_{org}) aerosol components. The sum of these two (W_{inorg}+W_{org}) equal to the total particle water is then compared to the LWC determined by the two nephelometers operating in dry and wet mode, respectively. Predicted aerosol water was compared to LWC determined from ambient versus dry light scattering coefficients. At Finokalia the sum of W_{inorg} and W_{org} was highly correlated and in close agreement with the measured LWC (on average within 10%), with slope=0.92 and R^2=0.8 for the whole measurement period (n=5201 points). As expected, the highest fine aerosol water values are observed during nighttime, when RH is also at its maximum, resulting in significant water uptake. W_{org} shows a significant diurnal variability with morning and afternoon average mass concentrations being 10-15 times lower than nighttime concentrations. Thus, during daytime W_{inorg} is the main form of particle water as the average values for the predicted water (W_{org}+W_{inorg}) are very close to the ones of the inorganic water alone. On the other hand, during nighttime, the contribution of organic water to the total aerosol water increases becoming significant during nighttime, when the photochemical activity and temperature are minimum. The average concentration of total aerosol water was found to be 2.19±1.75 μg m^{-3}, which according to the dry mass measurements, can contribute on average up to 33% of the total submicron mass concentration. The average aerosol water associated with organics, W_{org}, was found to be 0.56±0.37 μg m^{-3}, which constitutes about 27.5% of the total calculated water. The overall uncertainty of this calculation is estimated to be around 30%.

Based on aerosol water, particle pH is also calculated, a parameter which is very important for the atmospheric implications of aerosols but is difficult to measure directly. In the eastern Mediterranean during the studied period, aerosol pH varied from 0.5 to 2.8 indicating that the aerosol was highly acidic throughout the period. Biomass burning aerosol presented the highest values of pH in the submicron fraction and the lowest values in total water mass concentration. Interestingly enough, the value of 2.8 for biomass burning pH is well above the value of 2, which is a lower limit for the occurrence of nitrate's condensation. The correlation, which has been observed during fire events between biomass burning organic aerosol and particulate nitrates, may be explained by these pH levels, which favor nitrate condensation. It can be seen that, in general, for anthropogenic-laden air masses (e.g. from Istanbul, Black Sea and Continental Europe) aerosol mass resides mainly in the submicron aerosol (60-70%) and thus the submicron fraction seems also to drive the pH of PM_{10}, while most of the aerosol water (~70%) is present in the coarse fraction. pH is driven by the fine mode while on the contrary, the grand majority of the aerosol water is present in the coarse mode. This may be due to the important contributions of the hygroscopic sea salt components in the coarse mode and of the less hygroscopic organics in the fine mode.

In terms of mass concentration, the air masses affected by the two natural sources, namely of marine and dust origin, contain the largest amounts of total submicron water. Even though total water exhibits the highest mass concentrations for the specific sources, the relative contribution of organic water to the submicron fraction is the lowest (~19% for dust and ~15.5% for marine). For these two natural sources, the ratio between submicron pH and calculated pH for the PM_{10} fraction is the lowest observed, 30±17% (median 25%) and 6±19% (median 5%).

The low pH values observed during the studied period in the submicron mode and independently of air masses origin could have significant implications for nutrient availability and especially for P solubility which is the nutrient limiting sea water productivity of the eastern Mediterranean.

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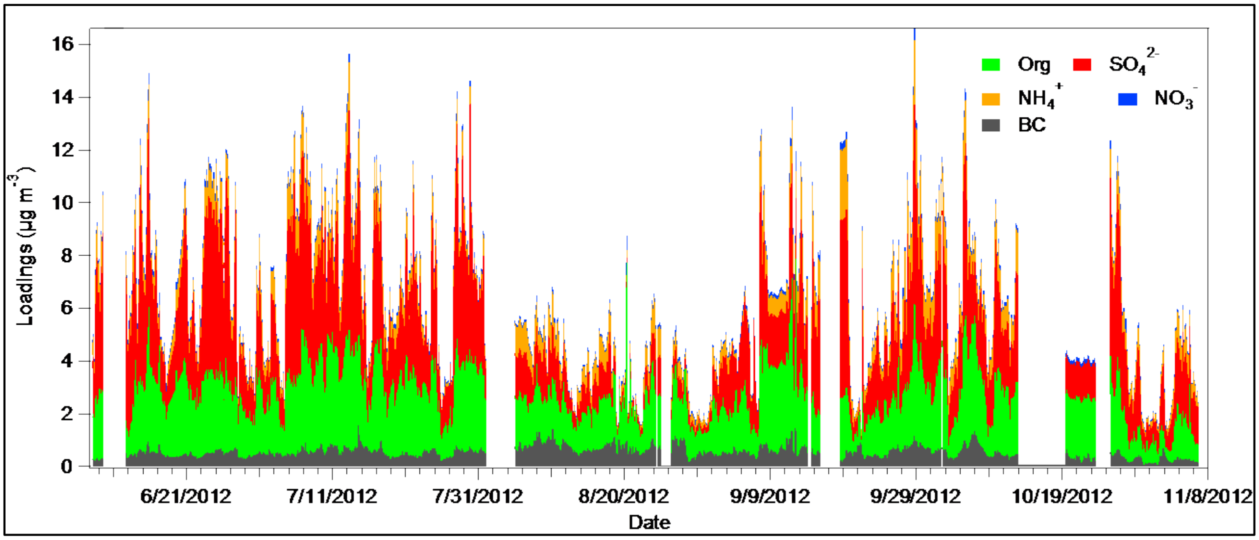

Figure 1: Time series of the main submicron aerosol components at Finokalia, Crete, during the measurement period in 2012.

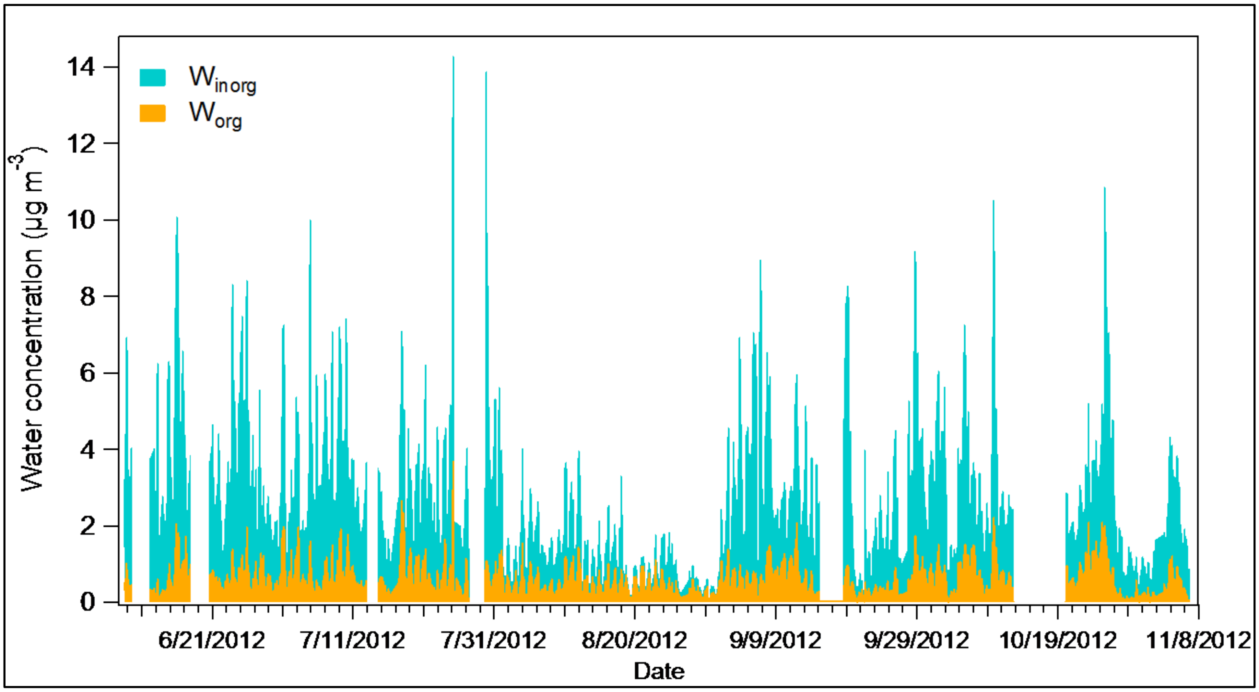

Figure 2: Time series of the two calculated aerosol water components, the water associated with the inorganic (W_{inorg}) and the organic (W_{org}) aerosol components.

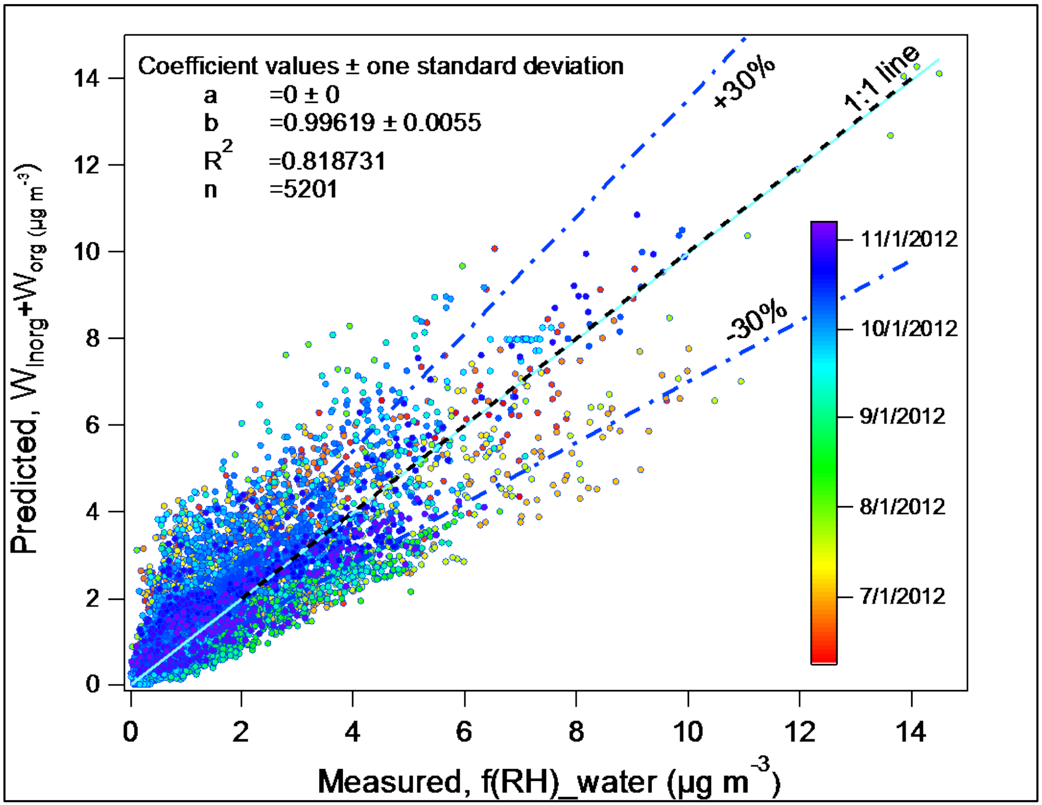

Figure 3: Correlation between calculated and measured LWC of aerosol.

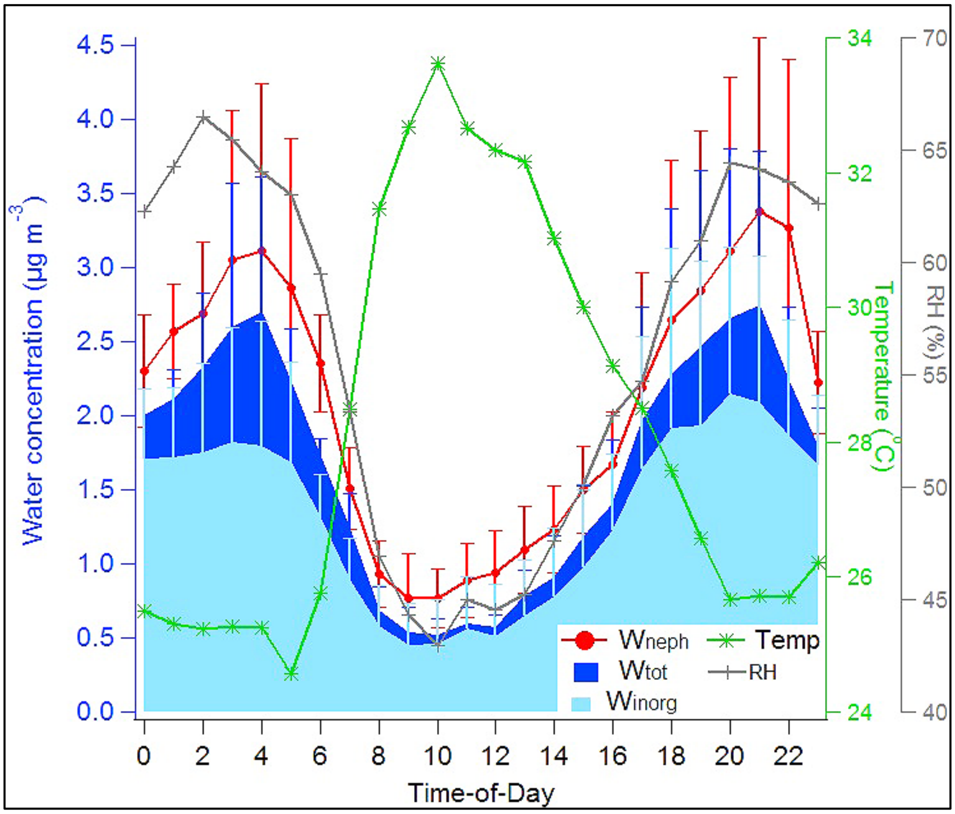

Figure 4: Diurnal profiles of predicted and measured water, along with measured RH and T. Average hourly averages and standard deviations plotted as error bars in local hour are shown.

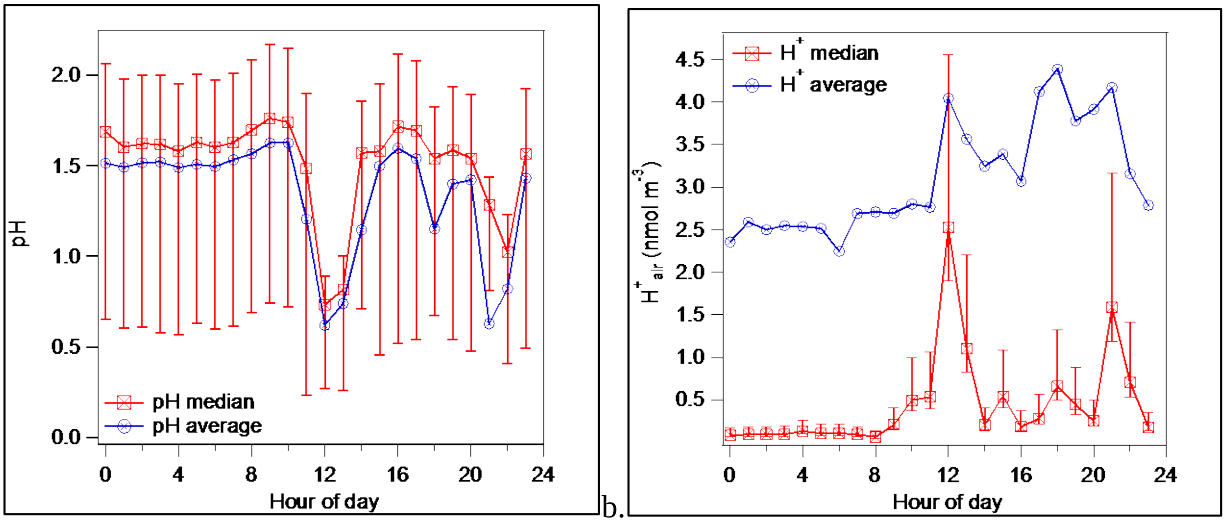

Figure 5: Diurnal profile of pH (a) and H^+ (b) calculated based on total predicted water and hydronium concentrations predicted by ISORROPIA-II. Average and median (with 25%, 75% quantiles) values are provided.

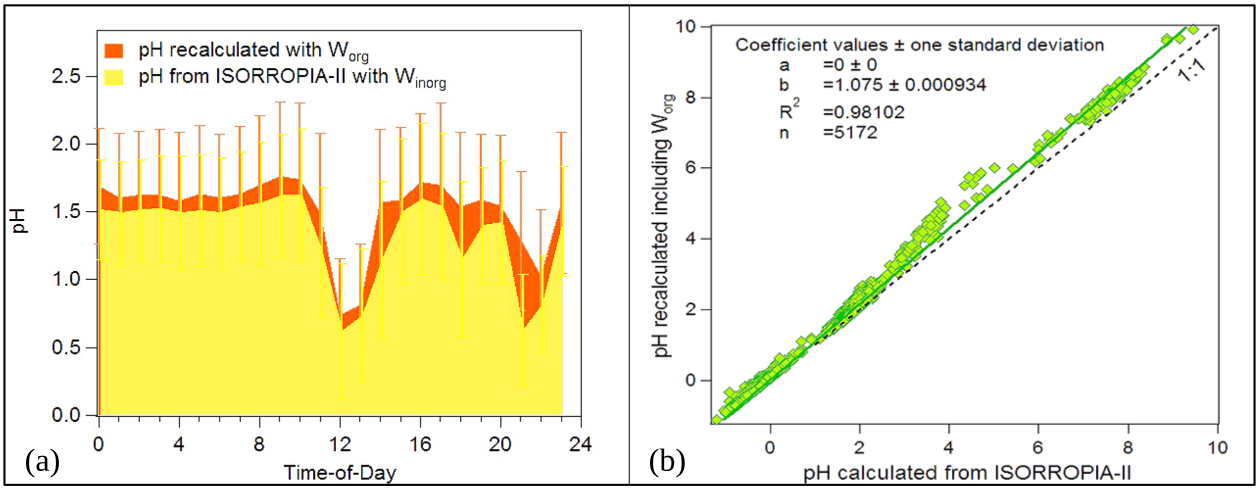

Figure 6: a) Diurnal variability of pH based on total predicted water (orange using both W_{org} and W_{inorg}) and only the inorganic water (yellow using only W_{inorg}), respectively. Average hourly values and standard deviation in the form of error bars are provided, b) Comparison between the pH predicted by ISORROPIA-II based on inorganic aerosol composition and that recalculated including also the organic component.

Table 1: Average values of water content (total and organic) and pH with standard deviation and median values in parenthesis.

	PM_1			**PM_1/PM_{10}**		
Source / region	**water$_{tot}$ (μg m^{-3})**	**water$_{org}$ (μg m^{-3})**	**pH**	**mass**	**water$_{tot}$**	**pH**
Biomass Burning (n=7)	1.33±1.22 (1.56)	0.37±0.33 (0.39)	2.77±0.88 (2.67)	0.48±0.16 (0.47)	0.08±0.09 (0.05)	0.89±0.2 (0.93)
Istanbul & Black Sea (n=7)	1.72±0.54 (1.21)	0.81±0.34 (0.75)	1.92±0.24 (2.00)	0.72±0.09 (0.69)	0.33±0.21 (0.26)	0.94±0.67 (0.88)
Continental Europe (n=9)	1.52±0.64 (1.32)	0.48±0.34 (0.47)	1.30±0.19 (1.26)	0.60±0.18 (0.64)	0.31±0.17 (0.28)	0.58±0.47 (0.50)
Dust (n=7)	2.48±0.54 (2.44)	0.48±0.22 (0.39)	1.48±0.44 (1.59)	0.34±0.08 (0.38)	0.39±0.08 (0.29)	0.30±0.17 (0.25)
Marine (n=7)	2.38±1.24 (1.91)	0.37±0.17 (0.34)	0.44±0.67 (0.43)	0.58±0.27 (0.57)	0.83±0.6 (0.70)	0.06±0.19 (0.05)